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ALKYL HALIDE HYDROLYSIS IN AQUEOUS ALCOHOL-WATER MIXTURES

CORRELATION BETWEEN ACTIVATION PARAMETERS AND PARTIAL MOLAL QUANTITIES OF THE SOLVENT

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)
A method has been devised to correlate observed changes in the enthalpy of
activation of alkyl halide hydrolyses in alcohol-water solutions with
partial molar thermodynamic quantities of the solvent components. The
partial molar quantities in the past have been related to structural changes
in the alcohol-water mixtures. Thus, this correlation can be used to deduce
specific solvation changes taking place in the transition state of alkyl
halide hydrolysis in alcohol-water solutions.

It was generally observed that groups of the solvating alcohol species have
to be removed in the transition state with the number of alcohol molecules
removed increasing as the alkyl group grows larger. Water molecules
participate in the formation of the transition states of substrates contain-
ing primary or secondary carbon centers but do not____ (Cont. on reverse)

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18. SUBJECT TERMS (Cont.)

Water-alcohol mixtures

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participate in the transition state of tertiary carbon centers.

PREFACE

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CONTENTS

ALKYL HALIDE HYDROLYSIS IN AQUEOUS ALCOHOL-WATER MIXTURES-- CORRELATION BETWEEN ACTIVATION PARAMETERS AND PARTIAL MOLAL QUANTITIES OF THE SOLVENT

1.   INTRODUCTION

In the hydrolysis of alkyl halides in highly aqueous regions of alcohol-water mixtures, extrema in the observed enthalpy and entropy of activation with changes in solvent composition are often observed.[1-3] Numerous studies have tried to correlate solvent properties in the binary solvent system with these trends in enthalpies of activation.[4-7] The most general conclusions are as follows:

a.   In the highly aqueous region of alcohol-water mixtures, water structure has to break to form the transition state.[8] This causes the energy of activation to increase, but the increase becomes less marked at higher temperatures. The enthalpies of activation generally decrease as the mole fraction of alcohol increases, and the enthalpies of activation reach minima at a specific solvent composition which corresponds to the maximum structure of water. As alcohol content increases further, parts of the tightly-bonded water structure start to break and the trend is reversed.

b.   Both ΔH_s (heat of solution of alkyl halides)[5] and ΔH_m (heat of mixing of alcohol in water)[4] are important factors affecting the observed extremum behavior of observed enthalpy of activation; and similarly, the corresponding quantities in entropies affect entropy of activation.

c.   When the substrate changes from ground to transition state, its solvation shell contributes to the observed changes in activation parameters; the effect is most marked in hydrolysis of the SN1 nature. However, the specific structural changes involved in the reorganization step are difficult to determine.[2]

d.   As the size of the alkyl group of the alcohol com-
ponent increases, as in the case of t-butanol, unmixing of the two
solvent components (microheterogeniety) is suspected to be present
at a specific alcohol composition and temperature. This can
explain the observed extrema in enthalpies and entropies of activa-
tion at that specific composition.[9,10]

In this report we define the solvent structural changes
which occur as one goes from the ground state to the transition
state. We will show that the change in the enthalpy of activation
as the alcohol content changes can be determined from the partial
molal quantities of the solvent components. Published kinetic data
on the hydrolysis of alkyl halides in alcohol-water mixtures are
examined. *We then define the solvent structural changes that occur*
in the transition state of these hydrolysis reactions in mixed
solvents.

2.   MODEL

We first assume that the mechanism of the activation step
is as follows:

$$R' X \text{ (solvated)} + m\ H_2O \rightleftharpoons [R'....X....(H_2O)\ m]^{\neq} + n\ ROH \qquad (1)$$

Since the solubilities of most alkyl halides increase as alcohol
content increases,[5] we assume that the alkyl halide substrate is
solvated by alcoholic species (hydrogen bonded to water) in the
solvent system. In the activation process, additional water mole-
cules are expected to enter the solvation shell to assist the
halide group leaving and to react with the substrate.[11] Thus, some
solvating alcohol molecules must leave the ground state solvation
shell and give room to the entering water molecules. This unmixing
and mixing of the solvent component contribute to the enthalpy
changes in the activation step. The overall enthalpy change of
this chemical process is the observed enthalpy of activation:

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$$\Delta H^{\neq}_{obs} = \bar{H}_{R'X}{}^{\neq} - \bar{H}_{R'X}{}^{g} + n\bar{H}_{ROH} - m\bar{H}_{H_2O} \tag{2}$$

where $\bar{H}_{R'X}{}^{\neq}$ and $\bar{H}_{R'X}{}^{g}$ are the partial molal enthalpies of the solvated transition and ground states of the alkyl halide R'X, respectively.

By definition:

$$\bar{H}_{R'X}{}^{\neq} = \Delta H_s(\neq) + H^O_{R'X(\neq)} \tag{3}$$

$$\bar{H}_{R'X}{}^{g} = \Delta H_s(g) + H_{R'X(g)} \tag{4}$$

$$\bar{H}_{ROH} = \bar{L}_{ROH} + H^O_{ROH} \tag{5}$$

$$\bar{H}_{H_2O} = \bar{L}_{H_2O} + H^O_{H_2O} \tag{6}$$

where H^O is the molal enthalpy of the pure compound, and $\Delta H_s(\neq)$ and $\Delta H_s(g)$ are heats of solution of the transition and ground states of R'X, respectively. Substituting Equations (3) through (6) to Equation (2),

$$\Delta H^{\neq}_{obs} = \left[H^O_{R'X(\neq)} - H^O_{R'X(g)}\right] + n\bar{L}_{ROH} - m\bar{L}_{H_2O}$$

$$+ \left[\Delta H_s(\neq) - \Delta H_s(g)\right] + nH^O_{ROH} - mH^O_{H_2O} \tag{7}$$

again, let

$$\Delta H^* = H^O_{R'X(\neq)} - H^O_{R'X(g)}$$

$$\Delta(\Delta H_s) = \Delta H_s(\neq) - \Delta H_s(g)$$

Equation (7) becomes

$$\Delta H^{\neq}_{obs} = \Delta H^{*} + n\bar{L}_{ROH} - m\bar{L}_{H_2O} + \Delta(\Delta H_s) + nH^{o}_{ROH} - mH^{o}_{H_2O} \qquad (8)$$

As the composition of the bulk solvent changes from X_2 to $X_2 + \delta X_2$ (a small change),

$$\delta\left(\Delta H^{\neq}_{obs}\right) = \delta(\Delta H^{*}) + \delta(n\bar{L}_{ROH}) - \delta\left(m\bar{L}_{H_2O}\right) + \delta\Delta(\Delta H_s) \qquad (9)$$

where δ symbolizes the difference of a property between two solvent systems of different mole fractions.

Since the reaction mechanism remains the same when solvent composition changes, we can safely assume that the structure of the transition state remains the same. Therefore,

$$\delta(\Delta H^{*}) = 0$$

$$\delta(n) = 0$$

$$\delta(m) = 0$$

and

$$\delta\left(\Delta H^{\neq}_{obs}\right) = n\ \delta\left(\bar{L}_{ROH}\right) - m\ \delta\left(\bar{L}_{H_2O}\right) + \delta\Delta(\Delta H_s) \qquad (10)$$

The last term in Equation (10), $\delta\Delta(\Delta H_s)$, is the change in the difference of heats of solution between the ground and the transition states of the pure substrate accompanying a change in solvent composition X_2 to X_2':

$$\delta(\Delta H_s) = \Delta H_s(\neq) - \Delta H_s(g) - \left[\Delta H_s'(\neq) - \Delta H_s'(g)\right] \qquad (11)$$

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rearranging,

$$= [\Delta H_s(\neq) - \Delta H_s'(\neq)] - [\Delta H_s(g) - \Delta H_s'(g)] \qquad (12)$$

According to Arnett,[5] the ΔH_s for all solutes is endo-thermic in highly-aqueous alcohol-water mixtures relative to pure water. The value of ΔH_s increases as X_2 increases up to a specific value of X_2, often denoted the "magic mole fraction".[11] The value of ΔH_s becomes less endothermic as X_2 increases further. Since all solutes exhibit the same behavior, we conclude that the difference in heats of solution as X_2 changes is small and can be neglected. Thus, Equation (10) becomes

$$\delta \Delta H^+_{obs} = n\delta\left(\bar{L}_{ROH}\right) - m\delta\left(\bar{L}_{H_2O}\right), \text{ and} \qquad (13)$$

$$\Delta H^{\neq}_{obs} = C + n\left(\bar{L}_{ROH}\right) - m\left(\bar{L}_{H_2O}\right) \qquad (14)$$

where

$$C = \Delta H^* + nH^O_{ROH} - mH^O_{H_2O} .$$

Equation (14) is consistent with the observation that the partial molal enthalpies of the solvent components are more indicative of the structure of the solvent mixture than the excess heat of mixing.[7]

Ironically, Arnett measured the heats of solution of vari-ous solutes in alcohol-water mixtures in order to compute $\Delta H^{\neq}_{obs}$. Arnett thought that the key parameters were ΔH_s of the ground state and the transition state. Arnett calculated $\Delta H_s(\neq)$ of t-butyl chloride in ethanol-water mixtures from $\Delta H^{\neq}_{obs} - \Delta H_s(g)$ for t-butyl chloride. The calculated values of $\Delta H_s(\neq)$ showed a complex variation with solvent composition which conflicts with Arnett's

measurements that ΔH_s of all solutes, ionic to hydrophobic, follow the same pattern as solvent components change. Thus, we contend that Arnett's view that

$$\Delta H_{obs}{}^{\neq} = \Delta H_s(\neq) - \Delta H_s(g) \tag{15}$$

is incorrect because the contributions from the mixing and unmixing of the solvent components as one goes from ground state to transition state are ignored. We suggest that Equation (14) corrects this.

We now wish to introduce the quantity ϕL_2 defined as follows:

$$\phi L_2 = \bar{H}_2 - H_2^{\bullet} \tag{16}$$

which can be written as

$$\phi L_2 = \bar{L}_2 - \left(\bar{H}^{\bullet} - H^O{}_2\right) \tag{17}$$

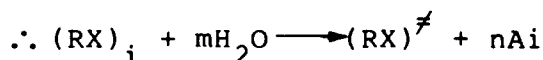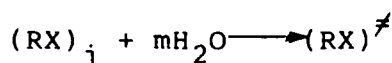where $\bar{H}^{\bullet}$ = the partial molal of enthalpy of component, Equation (2), in an infinitely dilute solution in water. Equation (14) can now be rewritten in terms of ϕL_2 as follows:

$$\Delta H_{obs}{}^{\neq} = C' + n\phi L_2 - m\bar{L}_{H_2O} \tag{18}$$

where $C' = \Delta H^{*} + n\bar{H}_2^{\bullet} - m\bar{H}^O{}_{H_2O}$

Basically, the difference between Equations (14) and (18) is that the standard state for alcohol is an ideal solution of an infinitely dilute alcohol-water mixture as opposed to a pure alcohol solution. In pure solvent, alcohol forms polymeric hydrates[8-10]

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A1, A2, ... Ai, where the magnitude of i depends on the mole fraction and the specific alcohol. We assume that a small amount of pure substrate, RX, can be added without disturbing the equilibrium among the polymeric hydrates. The substrate, RX, is solvated by various polymeric hydrates so that RX is the substrate solvated by alcoholic hydrate, i. We further assume that only a specific RX can form the transition state so that alcohol has to be removed to form the appropriate solvated substrate, i.e.:

$$(RX)_i \rightleftharpoons (RX)_j + nAi$$

$$(RX)_j + mH_2O \longrightarrow (RX)^{\neq}$$

$$\therefore (RX)_i + mH_2O \longrightarrow (RX)^{\neq} + nAi$$
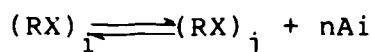
$(RX)^{\neq}$ rapidly forms products, and $\Delta H^{\neq}$ can be written as

$$\Delta H^{\neq} = \bar{H}(RX)^{\neq} - \bar{H}(RX)_i - m\bar{H}_{H_2O} + n\bar{H}_{Ai} \tag{19}$$

Here $\bar{H}_{Ai} = \phi L_2$, since ϕL_2 arises from the heat of dilution of the solvent mixture at X_2 to an infinitely dilute solution in which only the monomonic specie is present; ϕL_2 was calculated to be the average heat of formation of the polymeric alcohol species hydrogen bonded to water (alcohol-hydrates).[12] Therefore,

$$\Delta H^{\neq} = \bar{H}(RX)^{\neq} - \bar{H}(RX)_i - m\bar{H}_{H_2O} + n\phi L_2 \tag{20}$$

$$= \left[\bar{H}(RX)^{\neq} - \bar{H}(RX)_i - m\bar{H}^O_{H_2O} \right] - m\bar{L}_{H_2O} + n\phi L_2 \tag{21}$$

As X_2 changes, $\bar{H}(RX)^{\neq}$ and $\bar{H}(RX)_i$ remain the same since the reaction mechanism does not change. Thus,

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$$\Delta H^{\neq} = \text{constant} - m\bar{L}_{H_2O} + n\phi L_2 \qquad (22)$$

and the same relationship as Equation (18) is obtained.

We will try to demonstrate the relationship shown in Equation (18) for the following two groups of hydrolysis reactions:

● Group (A)--t-butyl chloride in methanol-water, ethanol-water, and t-butanol-water based on the data of Robertson and Sugamori[6] and of Moelwyn-Hughes.[13]

● Group (B)--four types of alkyl halides in one solvent system, t-butanol-water, based on published kinetic data for t-butyl chloride,[6] 1-adamantyl bromide,[14] cyclohexyl bromide,[14] and benzylchloride.[15]

In group (A), a tertiary carbon is present and the mechanism is SN1, while in group (B), various carbon centers from 1, 2, and 3 degrees to bridgehead carbon are compared in the same solvent system. The partial molal quantities of three alcohol-water systems are calculated from published data and listed in the Appendix.

3.   RESULTS AND DISCUSSION

The calculations based on Equations (14) and (18) are listed in Tables 1-3 for group (A) and Tables 4-6 for group (B) (Table 3 is common to both groups). In all cases, Equation (18) was found to fit the data better than Equation (14), except in Table 1. We believe this is because methanol does not associate as strongly as the rest of the alcohols under examination.[9] Since the methyl group is the least "hydrophobic" and methanol is the most polar among the alcohols, it may be that each single methanol molecule is hydrogen bonded to water molecules. This is shown in the smallest structure-promoting effect of methanol compared with larger alcohols.[8]

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Table 1. t-BuCl in MeOH-H_2O at 25 °C (A-1)[13]

X_2	$\Delta H^{\neq}_{obs}$ kcal/mole	$\Delta H^{\neq}_{obs} + 6L_1 - L_2$ kcal/mole
0.226	21.33	20.63
0.307	21.45	20.49
0.400	21.63	20.32
0.585	22.40	20.64
0.800	23.53	20.94

Table 2. t-BuCl in EtOH-H_2O at 10 °C (A-2)[6]

X_{EtOH}	$\Delta H^{\neq}_{obs}$ kcal/mole	$\Delta H^{\neq}_{obs} - n\phi L_2$ kcal/mole
0.075	22.05	23.17 (n=1/2)
0.110	21.21	23.19 (n=1)
0.150	20.09	23.26 (n=2)
0.250	21.55	23.24 (n=2)

Table 3. tBuCl in tBuOH-H_2O at 26 °C (A-3; B-1)[6]

X_{tBuOH}	$\Delta H^{\neq}_{26\ °C}$* kcal/mole	$\Delta H^{\neq}_{26\ °C} - n\phi L_2$ kcal/mole
0.02	21.36	23.30 (n=1/2)
0.05	16.25	22.01 (n=2)
0.10	20.13	23.04 (n=2)
0.20	22.30	23.43 (n=2)

*Calculated from $\Delta H^{\neq}$ at 10 °C and $\Delta Cp^{\neq}$ data;[6] $\Delta Cp^{\neq}$'s were assumed constant from 10 to 26 °C.

Table 4. 1-Adamantyl Bromide in tBuOH-H_2O at 38 °C (B-2)[14]

X_2	$\dfrac{\Delta H^{\neq}_{obs}}{kcal/mole}$	$\dfrac{\Delta H^{\neq}_{obs} - 4\phi L_2}{kcal/mole}$
0.08	22.11	27.73
0.10	23.30	27.76
0.15	25.19	27.93
0.20	26.35	28.11

Table 5. Cyclohexyl Bromide in tBuOH-H_2O at 38 °C (B-3)[14]

X_2	$\dfrac{\Delta H^{\neq}_{obs}}{kcal/mole}$	$\dfrac{\Delta H^{\neq}_{obs} - 2\phi L_2 + 2\bar{L}_1}{kcal/mole}$
0.05	21.41	25.61
0.08	23.19	25.76
0.10	23.88	25.86
0.15	24.83	25.91

Table 6. Benzylchloride in tBuOH-H_2O at 50 °C (B-4)[15]

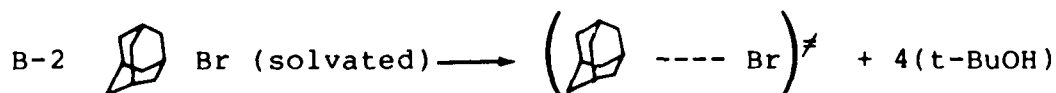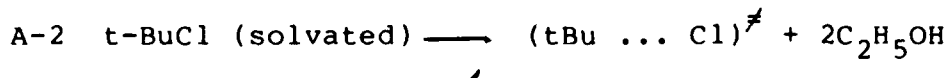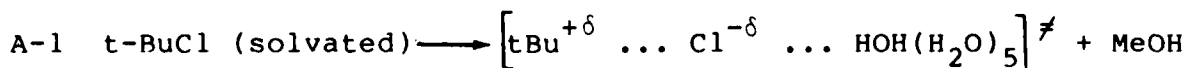| X_{tBuOH}	$\dfrac{\Delta H^{\neq}_{obs}}{kcal/mole}$	$\dfrac{\Delta H^{\neq}_{obs} - L_2 + 2\bar{L}_1}{kcal/mole}$
0.025	17.9	20.02
0.05	17.6	19.18
0.10	20.6	21.41
0.20	21.3	21.61
0.30	21.4	21.51

3.1   Cases When m = 0.

When water molecules are not present in the activation step, m equals 0 and the mechanism is pure SN1. The hydrolyses of t-BuCl in both $EtOH-H_2O$ (Table 2) and $tBuOH-H_2O$ (Table 3) and of 1-adamantyl bromide in $tBuOH-H_2O$ (Table 4) fall into this mechanism, since both substrates contain a tertiary carbon. Thus, the model correctly predicts the pure SN1 character.

3.2   The n Values.

To compare the n values among cases B-1 to B-4, it seems that n increases with the size of the alkyl groups in RX. This is consistent with our steric consideration that space for reaction with water is required and provided by the removal of solvated alcohol species from the substrate. The n value determined for each case remains constant over the X_2 range examined except at $X_2 = 0.02$ for case A-3. We will not speculate the reason for the change in n at $X_2 = 0.02$ in $tBuOH-H_2O$ at the present time.

3.3   Activation Steps.

We can write the transition state for each case based on the values of m and n:

A-1   t-BuCl (solvated) $\longrightarrow \left[tBu^{+\delta} \ldots Cl^{-\delta} \ldots HOH(H_2O)_5 \right]^{\neq} + MeOH$

A-2   t-BuCl (solvated) $\longrightarrow (tBu \ldots Cl)^{\neq} + 2C_2H_5OH$

A-3   t-BuCl (solvated) $\longrightarrow (tBu \ldots Cl)^{\neq} + 2(t-BuOH)$

B-2   Br (solvated) $\longrightarrow \left(\text{} ---- Br \right)^{\neq} + 4(t-BuOH)$

B-3 (cyclohexane with H) $\cdot$ Br (solvated) $\longrightarrow$ $\left(\begin{array}{c} \text{(cyclohexane)} \overset{+\delta}{\underset{H_2O}{\overset{H}{C}}} \text{- - - - }Br^{-\delta} \\ H_2O \end{array} \right)^{+}$ + 2(t-BuOH)

B-4 $\bigcirc$ CH_2Cl (solvated) $\longrightarrow$ $\left(\bigcirc - \overset{+\delta}{\underset{H_2O}{\overset{H}{C}}} \overset{H}{} \text{- - - - - - }\overset{-\delta}{\underset{H_2O}{Cl}} \right)^{+}$ + t-BuOH
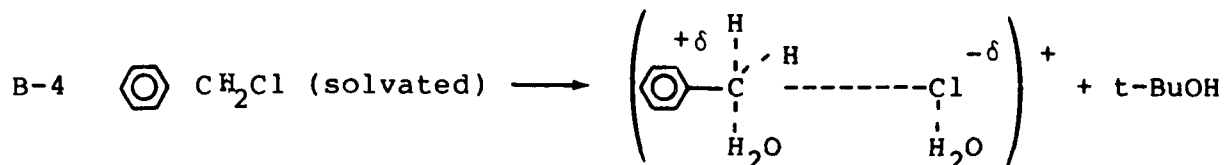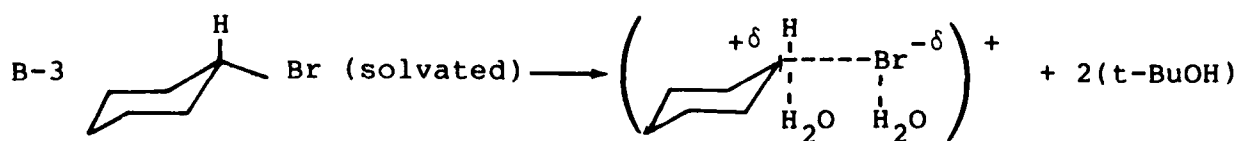
Note that all of the transition state complexes are also solvated
by the solvent system; presumably, the alkyl groups are surrounded
by the alcoholic-water groups. We are concerned with the change
in the solvation shell. The assumptions made in deriving Equations
(14) and (18) should be reemphasized here. The relationships may
not be applicable when

     a.   The reaction mechanisms or products change as solvent
composition changes.

     b.   The difference in the heats of solution (which
measure the extent of solvation) between the ground and the tran-
sition states of the alkyl halide substrate varies significantly
with solvent composition.

For reactions of more compxcex mechanisms than the typical

SN1 or SN2 model, additional patial molar enthalpy terms
may be required in Equations (14) and (18) to account for vari-
ations in $\Delta H^{\neq}$ with solvent composition. Similar contributions of
the quantities $\phi S_2^{\,e}$ and $\bar{S}_1$ to the observed $\Delta S^{\neq}$ are expected.

The relationship

$$\Delta S^{\neq}_{obs} = \text{constant} - m\bar{S}_1 + n\,\phi S_2^{\,e} \tag{23}$$

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was found to be true among some of the above cases (e.g., for cases B-2 and B-3)[14] but was not as satisfactory as our results for $\Delta H^{\neq}$, perhaps due to the greater uncertainties in obtaining the entropy data. However, since changes in enthalpy and entropy values are almost always compensatory, the same results should be expected for entropy of activation. We will not present our calculations for entropies in this report.

4. CONCLUSION

We have demonstrated a method to correlate the observed changes in $\Delta H^{\neq}$ for the hydrolysis of alkyl halides in aqueous alcohol-water mixtures with solvent composition to the structural-sensitive thermodynamic properties ϕL of alcohol and $\bar{L}$ of water. The correlation can further reveal the specific changes involved in the structure of the solvation shells at the activation step. As direct, microscopic evidences of the structures of the solvated ground and transition states of the alkyl halides are hard to obtain, the thermodynamic treatment of the kinetic data employed by this method provides an alternative approach to the understanding of the solvent structural changes accompanying the reaction. A general phenomenum was observed in all of the reactions analyzed-- that groups of the solvating alcohol species solvating the ground state have to leave to provide room for hydrolysis; the number of the leaving groups increases with the size of the alkyl group in the substrate. Water molecules participate in forming the transition states of substrates containing 1 or 2 degree carbon centers but are not present in the case of tertiary carbon.

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APPENDIX

PARTIAL MOLAL QUANTITIES OF ALCOHOL (2)

AND WATER (1) COMPONENTS IN ALCOHOL-WATER BINARIES

Table A-1. MeOH – H_2O at 25 °C[1]

X_2	$\bar{L}_2$ cal/mole	$\bar{L}_1$ cal/mole
0.226	-210	-152
0.307	-240	-200
0.400	-150	-243
0.585	-85	-303
0.800	-30	-437

Table A-2. EtOH – H_2O at 10 °C[2]

X_2	ϕL_2 cal/mole
0.075	-2240
0.110	-1981
0.150	-1586
0.250	-844

Table A-3. tBuOH – H_2O at 26 °C, 38 °C, and 50 °C[3]

X_2	ϕL_2			$\bar{L}_1$		
	cal/mole			cal/mole		
Temperature	26	38	50	26	38	50
0.02	-3885	--	-2495	--	--	--
0.025	-3710	--	-2120	-22	--	-17
0.05	-2880	-2180	-1606	-98	-78.7	-60
0.08	-1875	-1405	-1029	-157	-120	-88.5
0.10	-1453	-1113	-810	-170	-126.3	-92.0
0.15	-873	-685	-502	-184	-150	-117.0
0.20	-564	-442	-320	-195	--	-121.0

Appendix   26

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